

THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

Part III. The Spectrum of Light Scattering

BY SIR C. V. RAMAN

(*Memoir No. 128 of the Raman Research Institute, Bangalore-6*)

Received October 26, 1961

1. INTRODUCTION

IN the first part of this memoir, the modes of free vibration characteristic of the structure of rock-salt were described and it was shown how their frequencies could be computed. In the second part of the memoir, the activities of these modes in the absorption and reflection of infra-red radiation were discussed. Experimental data were presented which showed clearly that the normal mode of highest frequency is active not only as a fundamental but also as overtones of higher orders. The observed infra-red behaviour of rock-salt over a wide range of frequencies of the incident radiation was discussed and explained in terms of the activities of its characteristic modes of vibration.

The present part of the memoir is concerned with an entirely different spectroscopic technique which enables the existence of the discrete normal modes of vibration to be established and their frequencies as theoretically evaluated to be checked by comparison with the results of experiment. This technique makes use of the frequency shifts observed when monochromatic light traversing the crystal emerges after diffusion in its interior and the diffused radiation is examined spectroscopically. The intensity of the radiation so diffused is a very small fraction of that traversing the crystal. But this very circumstance makes the procedure one of the highest value for the purposes in view. For, the complications which are inherent in the use of infra-red radiation in the study of the spectroscopic behaviour of such an intensely absorbing material as rock-salt are entirely avoided. The spectroscopic picture of the crystal which emerges from the recorded spectra of the diffused light is very simple, clear and definite.

We shall begin with a few remarks of a general nature. The study of the diffusion of monochromatic light by the molecules of diatomic gases,

e.g., oxygen and nitrogen, gives us an insight into the origin of the frequency shifts in light-scattering. These shifts are readily identifiable with the characteristic vibrational frequencies of the molecules. The appearance of scattered radiations of altered wavelength is thus explicable as a consequence of a periodic variation in the power of the molecule to scatter light resulting from the relative movements of its atoms in such vibration. A similar explanation can be given for the frequency shifts observed in the diffusion of light by crystals, the structural units in the crystal instead of the molecules of the gas being regarded as the vibrating systems. The structural units in a crystal are held to fixed positions and cannot move freely in the manner of the molecules in a gas. This circumstance has necessarily to be taken into account in considering the dynamics of their vibrations. But in respect of the frequency shifts arising from their internal vibrations, the randomness of phase of the scattered radiations renders the situation not essentially different from that of scattering by the individual molecules of a gas.

2. SCATTERING OF LIGHT WITH DOUBLED FREQUENCY SHIFTS

As has been remarked above, the frequency shifts observed in the scattering of light may usually be identified with the vibrational frequencies of the scattering units. There is however a remarkable class of cases in which spectral shifts are observed having double the frequency of the vibrational modes which give rise to them. We may as an illustration mention the facts emerging from a study of the scattering of light in calcite. The CO_3 groups in that crystal have four internal modes of vibration. Three of them give frequency shifts of 712 cm^{-1} , 1086 cm^{-1} and 1436 cm^{-1} which may be identified respectively with the frequencies of three possible modes of vibration of the CO_3 group in its own plane. We are here concerned with a fourth frequency shift of 1749 cm^{-1} which is recorded with an intensity about equal to that of the 1436 cm^{-1} shift.

Now, the fourth mode of vibration of the CO_3 group is an out-of-plane movement in which the C atom oscillates along a line perpendicular to the O_3 group and finds itself alternately above and below the plane of the group. Such an oscillation may be expected to be strongly active in the absorption of infra-red radiation. Actually, a well-defined peak appears in the infra-red absorption spectrum of calcite at about 874 cm^{-1} and this is identified as arising from just such a vibration. But no line having that frequency shift or anywhere near it is recorded in the spectrum of the scattered light. We are thus obliged to infer that the frequency shift of 1749 cm^{-1} arises from

the infra-red active vibrational mode but is recorded in the scattering of light with double its frequency.

A doubling of the frequency shift in light-scattering as compared with an infra-red absorption frequency may be explained in the following manner. The infra-red activity arises from the movements of the electron clouds in the crystal. These movements have necessarily the same frequency as the movements of the atomic nuclei. In the scattering of light, however, we are concerned with the optical polarisability of the entire electronic cloud and this depends on its geometric configuration. In the particular case of the CO_3 group in calcite it is clear that the configuration of the group takes the same form twice in each oscillation. The periodic variation of optical polarisability has therefore twice the frequency of the vibration and hence the resulting frequency shift is also doubled. What is specially remarkable is that its intensity is comparable with those of the frequency shifts of the ordinary kind due to the other modes of vibration and that it is far greater than the intensity with which a shift of 2173 cm.^{-1} (double that of the planar oscillation of 1086 cm.^{-1}) is recorded in the spectrum.

3. THE ROCK-SALT SPECTRUM

We proceed to show that an effect of the same general nature as that considered and explained above in the case of calcite is exhibited by all the nine normal modes of vibration of the rock-salt structure. We may begin by considering the triply degenerate mode of highest frequency which is highly active in the absorption of infra-red radiation. In this mode the sodium and chlorine nuclei with their associated electronic clouds move in opposite phases with amplitudes inversely proportional to their masses. *Twice* in each oscillation, a chlorine nucleus comes closest to a sodium nucleus either from one side or from the other. In such an approach, the power of the NaCl group to scatter light is notably increased beyond what it is when the Na and Cl nuclei are separated by their normal spacing in the crystal. Accordingly, the periodic variations of the scattering power of the NaCl groups in the crystal have *twice* the frequency of the vibrational mode. The frequency shift to which it gives rise is therefore also of double frequency. A component having the same frequency as the vibrational mode is totally absent, since the approach of a chlorine nucleus to a sodium nucleus is balanced by the recession of a chlorine nucleus from the same sodium nucleus on the opposite side. In other words, the vibrational mode is antisymmetric with respect to each sodium nucleus and each chlorine nucleus in the assembly. It is therefore inactive in light-scattering in the sense of the term as ordinarily understood.

The same argument may be extended to the four other coupled oscillations of the Na and Cl nuclei. Two of these modes are tangential and the two others normal to the cubic layers in the crystal; in all these cases, the movements in alternate layers are in opposite phases. In the tangential mode designated in the earlier parts of this memoir as II (*a*), the Na and Cl nuclei approach and recede from each other in much the same manner as in the mode I discussed above. The alternation in phase from layer to layer leaves the argument unaffected; for, at the instant when the Cl and Na nuclei are closest to each other in one layer, they would also be closest to each other in the next layer. It follows that mode II (*a*) would be active in the double-frequency modified scattering of light to much the same extent as the principal mode already considered. Indeed, mode II (*a*) having a degeneracy of six may be expected to exhibit a greater intensity than mode I which is only triply degenerate.

Considering next the tangential mode designated as II (*d*) in which the Na and Cl nuclei in each cubic layer oscillate in the same phase, the phases of the movements being reversed in the successive layers, it is evident that the double-frequency effect would also arise in respect of this mode but it would be very much feebler. For, the movements of the Na and the Cl nuclei being in the same phase, their approaches to each other would necessarily be much less close than when the movements are in opposite phases. The periodic fluctuations in the scattering power of the NaCl groups would therefore be relatively small and hence the observable effect of mode II (*d*) as recorded in the spectra of the scattered light should be far less conspicuous.

Arguments of the same kind may be extended to the consideration of the activity of the triply degenerate oscillations of the Na and Cl nuclei normal to the cubic planes designated as modes II (*b*) and II (*c*) respectively. In mode II (*b*) the Na and Cl nuclei move in the same phase and this has the higher frequency, while II (*c*) in which they move in opposite phases has the lower frequency. But the approaches between the Cl and Na nuclei which give rise to an increased scattering power are those between the nuclei which are in adjacent layers. Hence, it follows that the mode II (*b*) of the higher frequency would be much more strongly active than mode II (*c*) of the lower frequency. Since both the modes are only three-fold degenerate, their recorded intensities would be low. In particular, the mode II (*c*) of lower frequency would be recorded only very feebly.

4. ACTIVITY OF THE OCTAHEDRAL MODES

We now proceed to discuss the activity of the modes in which the Na nuclei alone, or the Cl nuclei alone oscillate. The layers containing them

are the octahedral planes of the crystal and the movement is either perpendicular or parallel to those planes, its phase being reversed in the successive layers. The oscillations perpendicular to the octahedral planes have a degeneracy of four and the nuclei move along the body-diagonals of the cube. The oscillations tangential to those planes have a degeneracy of eight and the nuclei move along one or another of the two-face diagonals appearing in the octahedral planes.

We proceed to consider the nature of the movements in these modes. In the perpendicular modes, a nucleus would approach its three nearest neighbours on the one side and recede from its three nearest neighbours on the other side. In the parallel modes, a nucleus would approach two of its nearest neighbours on one side and recede from two of its nearest neighbours on the other side. In either case, the movements would not give rise to frequency-shifts in light-scattering of the usual kind. They would, however, all be active in the modified scattering of double frequency. The parallel movements, being twice as numerous, may be expected to be recorded with greater intensity than the perpendicular ones.

We may summarise the overall picture which emerges from the foregoing considerations regarding the spectroscopic behaviour of rock-salt in light-scattering as follows:

- (a) All the nine normal modes would exhibit a doubled frequency shift but with very different intensities.
- (b) The triply degenerate mode of highest frequency would be strongly recorded but would be inferior in intensity to the cubic mode of lower frequency similar to it in character but which is six-fold degenerate.
- (c) The two cubic modes of low frequency would be recorded only feebly, the one which is three-fold degenerate even more weakly than the other of lowest frequency which is six-fold degenerate.
- (d) The eight-fold degenerate oscillation of the chlorine nuclei tangential to the octahedral planes should appear with notable intensity as a conspicuous feature in the spectrum, being adjacent to the two feebly recorded modes of lowest frequency.
- (e) The eight-fold degenerate oscillation of the sodium nuclei parallel to the octahedral planes would be recorded more strongly than the four-fold degenerate movement perpendicular to those planes.

5. THE SPECTRUM OF LIGHT SCATTERING

The vibration frequencies of the five cubic modes involving coupled oscillations of the Na and the Cl nuclei were listed in an earlier part of this memoir. To this list we must now add the frequencies of the four octahedral modes in which only the Na or only the Cl nuclei oscillate. As a rough approximation, the frequencies of these modes can be expressed in terms of the infra-red active mode of highest frequency by replacing the reduced mass of the two nuclei in its formula by the mass of the Na nucleus alone or of the Cl nucleus alone. But, as already remarked upon and explained in the first part of the memoir, the values thus obtained need correction and their frequencies have to be increased by amounts which are greater for the perpendicular vibrations than for the parallel ones. The corrected frequencies are most conveniently determined from the spectral shifts observed in light scattering, as they are readily identified in those spectra.

TABLE I

Modes and frequencies (cm.⁻¹)

Modes	De- gene- racy	Princi- pal mode	Cubic class	Octa- hedral class	Doubled fre- quency	Intensity
I	3	180 (NaCl)	360	Moderate
III (a)	4	170 (Na)	340	Moderate
III (b)	8	157 (Na)	314	Strong
II (a)	6	..	150 (NaCl)	..	300	Strong
III (c)	4	140 (Cl)	280	Strong
II (b)	3	..	129 (NaCl)	..	258	Weak
III (d)	8	117.5 (Cl)	235	Intense
II (c)	3	..	110 (NaCl)	..	220	Very weak
II (d)	6	..	92 (NaCl)	..	184	Weak

Table I gives the frequencies of all the nine normal modes. Their degeneracies and descriptions are also shown. They have been entered in Table I in the descending order of frequency. The doubled frequency

shifts in light scattering appear in the penultimate column. The entry against each frequency shift under the head intensity is based on the indications of theory, *viz.*, the degeneracy of the mode and the nature of the movements involved. These considerations have already been discussed in detail above and need not therefore be repeated here.

6. THE CONSEQUENCES OF THERMAL AGITATION

It is a familiar experience in studies on the scattering of light in crystals to find that the observed frequency shifts exhibit a thermal effect. The lines sharpen and the frequency shifts show a readily measurable increase when the crystal is cooled down to liquid air temperature. When, on the other hand, the crystal is warmed up, the lines become more diffuse as the result of an asymmetrical broadening. As a consequence of such broadening, the frequency shifts also diminish. The effects of this nature are both absolutely and relatively more conspicuous in the case of the vibrational modes of low frequencies. As examples may be mentioned the behaviour of calcite and of quartz in which they have been very fully studied. A thermal broadening and the accompanying diminution of the frequency shifts would necessarily occur also in the case of rock-salt. Since we are concerned with double-frequency scattering, they would be magnified two-fold. On the basis of the known data for quartz and calcite we may expect a broadening of the lines in the spectrum of rock-salt of about ten wave-numbers.

It follows from what has been stated that in the crowded spectrum indicated by the figures in Table I, the thermal broadening would result in the resolution of the frequency-shifts which are not very different becoming distinctly imperfect. When, however, a strongly recorded frequency shift has only weak companions on either side, its character as a discrete line-shift would be more clearly apparent.

7. COMPARISON WITH THE EXPERIMENTAL RESULTS

With a crystal of rock-salt five centimetres thick which was illuminated by the extremely intense ultra-violet radiation at λ 2536.5 emitted by a water-cooled magnet-controlled mercury arc in quartz and giving an exposure of 8 hours, Rasetti obtained a remarkable spectrogram. This was published with a microphotometer record of the spectrum alongside of it. An enlargement of this microphotometer curve copied directly from Rasetti's original publication is reproduced below as Fig. 1 in the text.

A special method was employed by Rasetti to prevent the complete fogging of the photographic plate which would have otherwise resulted from

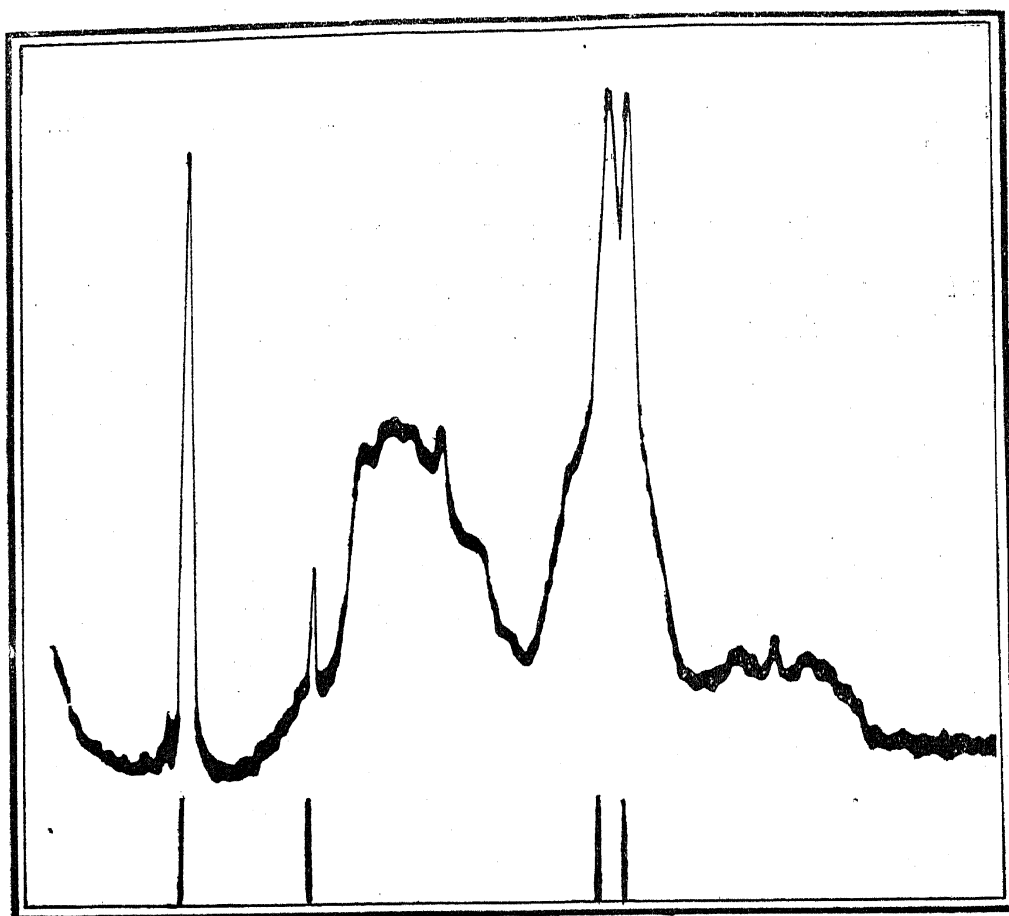


FIG. 1. Microphotometer Record (after Rasetti).

such prolonged exposure to intense illumination. A filter of mercury vapour was introduced which absorbed the $2536\cdot5$ radiation entering the instrument before it reached the photographic plate. A remarkably clear and well-exposed spectrogram was thus obtained. Neither the accompanying λ 2535 radiation nor the faint continuum extending to about 50 wave-numbers on either side of λ $2536\cdot5$ is cut out by the filter. They are recorded on the spectrogram, but have no significance.

The frequency shifts which arise from the scattering of the $2536\cdot5$ radiation in rock-salt are all found to lie between the limits 360 cm.^{-1} and 184 cm.^{-1} indicated by the theory. Beyond these limits, the spectrum falls off steeply in intensity. The fall on both sides would have been even steeper had the inevitable background of continuous spectrum which is an accompaniment of the monochromatic radiations of the mercury arc been totally absent in the record. But such absence could scarcely have been hoped for in view of the prolonged exposures necessary to obtain the spectrum.

For the convenience of the reader, the original spectrogram of rock-salt has been reproduced in a somewhat enlarged form as Fig. 1 in Plate VII accompanying the present memoir. On an inspection of the spectrum, it is evident that it presents precisely those features which would result from the nine double-frequency shifts listed in Table I being recorded in the positions and with the relative intensities listed in Table I. On closer examination, it becomes clear that the correspondence between the observed spectrum and the theoretical conclusions listed in Table I extends to all the observable details in it. The experimental conditions, *viz.*, the small dispersion of the spectrograph and the broadening of the frequency-shifts by the thermal agitation in the crystal are unfavourable to a complete resolution of the nine frequency shifts from each other. Nevertheless, it is clear that they are all present and have the positions and relative intensities indicated by the theory.

We may begin by referring to a striking feature in the spectrogram, *viz.*, the well-defined frequency shift of 235 cm.^{-1} which stands out in the record on both sides of the exciting radiation. The shift appears in a part of the spectrum where the frequency shifts on either side are weak or very weak as indicated by the theory and also as actually observed. Naturally, therefore, the 235 cm.^{-1} frequency shift is permitted to exhibit its true character as a discrete line-shift. It is not surprising also that the intensity of the shift due to the eight-fold degeneracy of the vibration makes it a prominent feature in the spectrum.

The two lowest frequencies listed in Table I are coupled oscillations of the Na and the Cl nuclei appearing in the cubic planes. The theory indicates that they would appear in the spectrum with a much lower order of intensity than the other modes, the reason being the Na and Cl nuclei have the same phase of vibration and cannot therefore make close approaches to each other. The two modes should also differ in their relative intensities by reason of the degeneracies being different, being three and six respectively. These consequences of the theory are in striking accord with the experimental facts. Actually, the frequency shifts of 220 cm.^{-1} and 184 cm.^{-1} are by far the feeblest recorded in the spectrum. The shift of 220 cm.^{-1} is, in particular, so weak as scarcely to be visible in the reproduction of the spectrum. Its presence in the microphotometer record can be made out with some difficulty being obscured by the steep rise in the intensity as we approach the intense 235 cm.^{-1} shift. The shift of 220 cm.^{-1} can, however, be readily recognised in the microphotometer record on the "anti-stokes" side of the spectrum as a second and weaker hump between the 184 cm.^{-1} and 235 cm.^{-1} shifts. (Figure 1 in the text, right-hand side of the microphotometer curve.)

It is a significant consequence of the theory that the smaller frequency shift of 300 cm.^{-1} should be recorded with twice the intensity of the larger shift of 360 cm.^{-1} by reason of its higher degeneracy, though the oscillations are very similar to each other in character. That this is actually the case is clear from the spectrogram itself. In the microphotometer record (Fig. 1 in the text, left-hand side of the curve), the frequency shift of 300 cm.^{-1} stands at a much higher level than 360 cm.^{-1} . It is well known, however, that differences in intensity between the different lines in a spectrogram are better appreciated when the exposure is not very heavy, as the photographic blackening is then not too great to show up the gradations in exposure. Likewise, for a microphotometer record, a moderately exposed plate is more suitable than a heavily exposed one. For, in the latter case, the differences of intensity are greater reduced in the transmission through the blackened plate which is recorded photometrically.

The importance of the foregoing remarks will be realised on an examination of the microphotometer record reproduced above in the text as Fig. 1. Rasetti's spectrogram and its microphotometer trace show the spectral shifts recorded on both sides of the exciting radiation $\lambda\ 2536.5$. On the "anti-stokes" side, the exposures are much less heavy and hence its microphotometric record is better suited to exhibit the relations of intensity between adjacent parts of the spectrum than the record of the more heavily exposed spectrum on the other side.

It has been already remarked that the 220 cm.^{-1} shift which is only vaguely indicated on the heavily exposed side of the record is quite clearly seen on the "anti-stokes" side. Likewise, all the frequency shifts listed in Table I are clearly visible on the "anti-stokes" side of the microphotometer record distinctly separated from each other. Instead of the 360 cm.^{-1} and 340 cm.^{-1} shifts appearing fused into a single band as on the heavily exposed side, they are seen on the "anti-stokes" side quite clearly as two distinct steps one above the other. The third step which is visible in the record is the 314 cm.^{-1} shift. Two other strongly recorded shifts, *viz.*, 300 cm.^{-1} and 280 cm.^{-1} , are seen higher up in the photometer curve. The weak 258 cm.^{-1} shift appears as the drop in intensity which immediately precedes the strongly recorded peak shift of 235 cm.^{-1} . Thus, the microphotometer record on the "anti-stokes" side enables us to recognise all the nine frequency shifts individually and to appreciate the great differences in intensity which they present more clearly than the record on the heavily exposed side permits.

We may sum up the foregoing by stating that the experimental results completely establish the correctness of our theoretical approach and are a

verification of the various observable consequences to which the theory points.

8. SUMMARY

All the nine normal vibrational modes of the rock-salt structure can give frequency shifts in light-scattering which are twice their respective frequencies but are of very different intensities, determined by their degeneracies and the nature of the movements of the Na and Cl nuclei in those modes. The doubled frequencies in cm^{-1} with their respective degeneracies are 360 (3), 340 (4), 314 (8), 300 (6), 280 (4), 258 (3), 235 (8), 220 (3), 184 (6). The spectroscopic facts are in full agreement with the theoretical deductions.

APPENDIX

REFLECTION AND TRANSMISSION OF LONG WAVES

The frequencies of the characteristic vibrational modes of the rock-salt structure determined spectroscopically and expressed as infra-red wavelengths are the following: $55.6\ \mu$, $58.8\ \mu$, $63.7\ \mu$, $66.7\ \mu$, $71.4\ \mu$, $77.5\ \mu$, $85.0\ \mu$, $90.9\ \mu$ and $108\ \mu$. The question arises of the part they play in the reflection by rock-salt surfaces and in the transmission through thin films of long-wave infra-red radiation.

Amongst these modes, that of the highest frequency with the characteristic wavelength $55.6\ \mu$ stands in a class apart by itself, being the strongly infra-red active fundamental. It is therefore to be expected that this mode would play a dominating role in the reflection of infra-red radiation and that it would also manifest itself as the principal cause of absorption in thin films.

The reflecting power of rock-salt actually reaches its maximum value of about 90% at a wavelength which is nearly the same as that of its active fundamental. But it is considerable both at shorter and at longer wavelengths. On the long wavelength side, the reflecting power diminishes progressively and reaches a limiting value of 20% at and beyond $100\ \mu$. On the short wavelength side, the reflecting power drops off more quickly and becomes quite small at about $33\ \mu$. There are indications of a minor maximum of reflecting power at about $38\ \mu$.

That the reflecting power at shorter wavelengths is considerable is readily explained. Four of the characteristic vibrational modes are coupled oscillations of the Na and the Cl nuclei in the crystal which are strongly infra-red active with a *doubled frequency*. The absorption wavelengths thus arising are $33.3\ \mu$, $38.8\ \mu$, $45.5\ \mu$ and $54.3\ \mu$ respectively. The existence of absorptions at these wavelengths is indeed demonstrable by observations with rock-salt plates with appropriately chosen thicknesses. Their co-operation with the active fundamental in infra-red reflection is a natural consequence. That the reflecting power becomes negligible at wavelengths less than $33\ \mu$ is only to be expected in these circumstances.

The existence of a whole series of normal modes of vibrations of the rock-salt structure with characteristic wavelengths ranging between $55\ \mu$ and $108\ \mu$ furnishes us with a clue to the explanation of the fact that the reflecting power of rock-salt diminishes only slowly in this range and reaches its

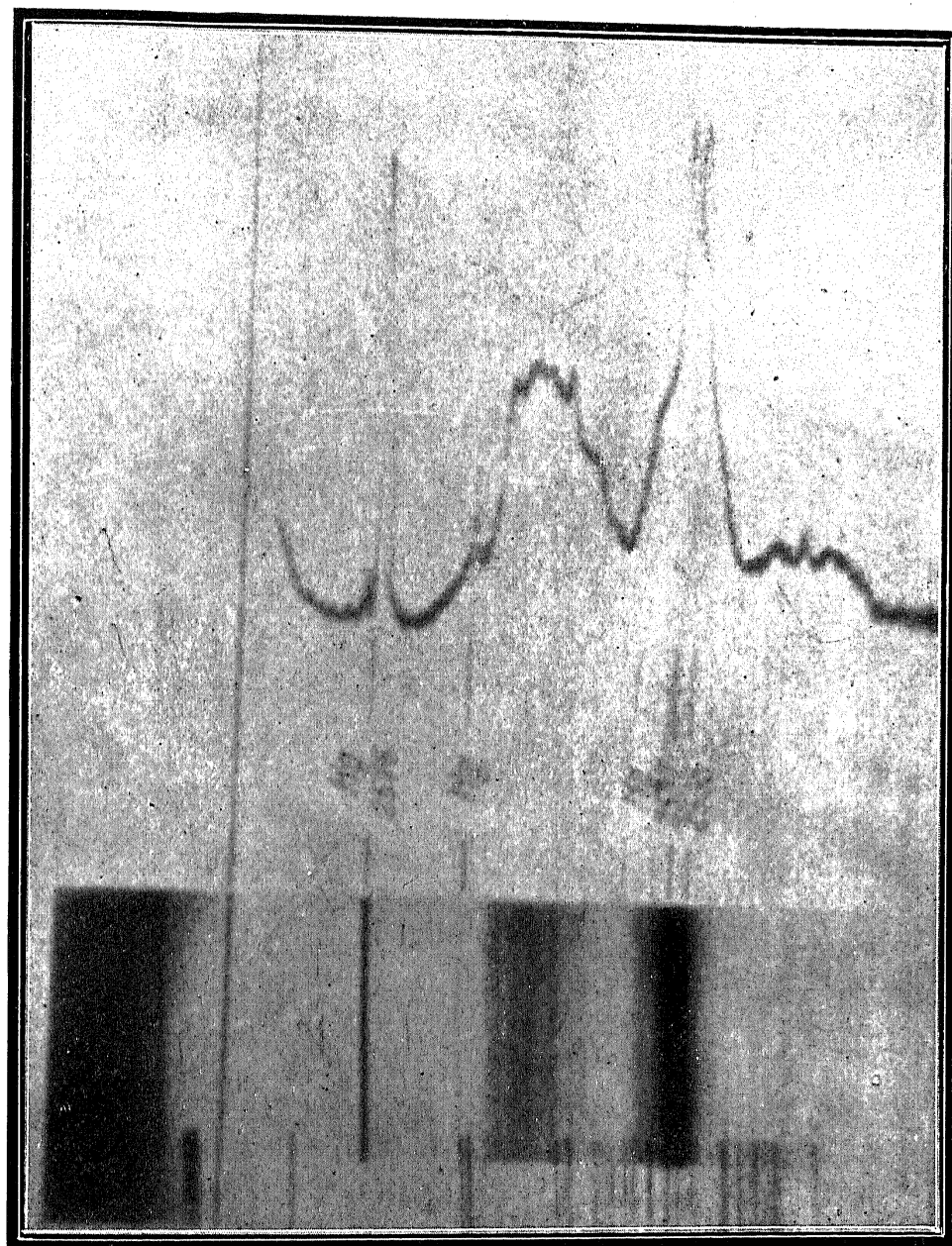


FIG. 1. Double-Frequency Shifts in Light-Scattering by Rock-Salt.

limiting value of 20% beyond $100\ \mu$. Infra-red activity arises from the movements of the electronic clouds in the crystal set up by the incident radiation. A complete independence of the normal modes of vibration and of their excitation cannot be assumed in these circumstances. That the different normal modes would co-operate to varying extents and that such excitation would manifest itself in the reflecting power of the crystal is only to be expected.

In determining the transmission by the thinnest films of NaCl, the fundamental absorption at $55.6\ \mu$ would naturally play the leading role. But one cannot ignore the existence of other absorptions which would simultaneously operate. Amongst these are the modes which are active with doubled frequencies as stated above. We should also take account of the whole series of modes with greater wavelengths which may be simultaneously excited by the reason of the non-independence of normal modes. It would not be surprising if in these circumstances the wavelength of maximum absorption is shifted appreciably towards wavelengths greater than $55.6\ \mu$.